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Tutor Marked Assignment
Atomic and Molecular Spectroscopy (MCH-020)

Course Code: MCH-020
Assignment Code: MCH-020/TMA/2026
Maximum Marks: 100

Note: Attempt all questions. The marks for each question are indicated against it.

You may use the following whenever required:
$h = 6.626 \times 10^{-34}\, Js$; $m_e = 9.11 \times 10^{-31}\, Kg$; $c = 3.0 \times 10^{8}\, ms^{-1}$

1. Answer ***any five*** of the following questions in brief: **(2X5)**

(a) Explain the origin of atomic spectrum.

(b) What is meant by anisotropy of chemical bond? Give an example.

(c) What makes TMS a molecule of choice to act as a reference in the NMR spectrometry?

(d) What is meant by polarizability of a molecule?

(e) In what way is NMR spectrometry different from other molecular spectroscopic methods?

f) What is the importance of ^{13}C-NMR spectroscopy in structure determination?

(g) What is the requirement of the vibrational mode of a molecule to be Raman active?

(h) What is the photoelectric effect? Write the equation of Einstein's photoelectric law.

2. **(a) (i)** 5G services in India are provided at a frequency of 3300 MHz. Calculate the wavelength of the radiation. **(2)**

(ii) Explain why the atomic spectra are line spectra whereas the molecular spectra are band spectra. **(3)**

(b) A photon of visible light has a wavelength of 550 nm. Calculate its **(5)**

(i) wavenumber

(ii) frequency

(iii) energy per mol

3. **(a)** What is meant by the Balmer series of hydrogen? What will be the wave number of the longest wavelength in the Balmer series? **(5)**

(b) A photoelectron spectrum of a compound containing nitrogen (N), aluminium (Al), and fluorine (F) shows three strong peaks at the following binding energies:

- Peak X: ~686 eV
- Peak Y: ~399 eV
- Peak Z: ~73 eV

Find the best option from the choices given below that best explains the relative positioning of these peaks in terms of binding energy.

(i) Peak X corresponds to F 1s electrons, which have the highest binding energy because fluorine's high electronegativity and small size give its 1s electrons a large effective nuclear attraction. Peak Y is N 1s and Peak Z is Al 2p.

(ii) Nitrogen has more valence electrons than fluorine or aluminium, therefore its peak appears at the highest binding energy.

(iii) The spectrum shows more aluminium atoms than nitrogen or fluorine, so its peak appears at the lowest binding energy due to dilution.

(iv) Aluminium has the highest nuclear charge, so its 2p peak should have the largest binding energy, but shielding effects reverse this trend.

Justify your answer. **(5)**

4. **(a) (i)** What information about the molecule can be obtained from a rotation spectrum? **(2)**

(ii) What is meant by a selection rule? Give the selection rule for a rotating diatomic molecule modelled as a rigid rotator. **(3)**

(b) Assuming that the force constants of H-Cl and D-Cl are the same, calculate the fundamental vibration frequency of D-Cl if that of H-Cl is 2890 cm^{-1}. **(5)**

5. **(a)** In Raman spectra, the Stokes line are more intense than the anti-Stokes lines. Why? **(2)**

(b) The rotational Raman spectrum of a diatomic molecule has the first line of a series of Stokes and anti-Stokes lines at 346 cm^{-1}, relative of the $\bar{\nu}$ of incident light. What would be its bond length. **(4)**

(c) CN^+ has bond length 129 pm. Calculate the wavenumbers of the first four lines in its microwave spectrum. **(4)**

[Given: mass of C=12.000 u and mass of N=14.007 u]

6. **(a) (i)** Calculate the number of vibrational modes for a molecule of methane. **(2)**

(ii) The frequencies of the first and second overtones respectively are exactly double and triple of the fundamental vibration frequency. Comment. **(3)**

(b) Raman rotational spectra of H_2 was observed with Hg light with Rayleigh line at 2294 cm^{-1}. Stokes lines were observed at 22581, 22337, 22094, 21851 cm^{-1}. Draw the rotational energy level diagram with Stokes and anti Stokes lines. **(5)**

7. **(a) (i)** Electronic transitions are called vertical transitions. Comment. **(2)**

(ii) A light source of wavelength λ illuminates a metal surface and electron are ejected with the maximum kinetic energy 2 eV. If the same surface is illuminated by a light source of wavelength $\lambda/3$, then calculate the maximum kinetic energy of the ejected electron. (Work function of metal is 1 eV) **(3)**

(b) (i) How does the rule of Mutual Exclusion help in predicting the symmetry in case of H_2O and CO_2 molecules? **(2)**

(ii) The molecule X_2Y has 3 fundamental vibrational frequencies. One is Raman active and two are IR active. Identify the structure of the molecule. **(3)**

8. (a) (i) Explain why the ^{13}C-^{13}C spin splitting is not observed in ^{13}C-NMR spectrum? **(2)**

(ii) Predict the number of signal and multiplicity of peaks in the ^{13}C spectrum of the following compounds: **(4)**

a) 2,5-Dimethylhexane

b) Cyclohexanol

(b) (i) What is meant by AX spin system in NMR? Draw a schematic energy level diagram for this system and show the allowed transitions. **(2+2)**

9. (a) (i) Calculate the ESR frequency of an unpaired electron in a magnetic field of 3000 G (0.3 T). **(2)**

[Given: g = 2.0023; $\mu_B = 9.2741 \times 10^{-24}\ JT^{-1}$; and h = $6.626\times10^{-34}\ Js$]

(ii) Which of the following systems will show electron spin resonance (ESR) spectrum? (i) H (ii) H_2 (iii) Na^+ (iv) Cl^- (v) $^{\bullet}CH_3$ (vi) NO_2 **(3)**

(b) What are different mechanisms that contribute to the relaxation of nuclear spins in the excited state? Explain any one of them. **(5)**

10. (a) (i) What is Mossbauer effect? **(2)**

(ii) The lifetime of ^{57}Fe (excited state) is 1.52 x 10^7 s. If the excited state is 14.3 keV above the ground state determine the linewidth τ and ratio τ /E. **(4)**

(b) Write short notes on the following. **(4)**

(a) Isomer shift (b) Spin-Spin splitting

1. Answer any five of the following questions in brief:

(a) Explain the origin of atomic spectrum.

(b) What is meant by anisotropy of chemical bond? Give an example.

(c) What makes TMS a molecule of choice to act as a reference in the NMR spectrometry?

(d) What is meant by polarizability of a molecule?

(e) In what way is NMR spectrometry different from other molecular spectroscopic methods?

(f) What is the importance of 13C-NMR spectroscopy in structure determination?

(g) What is the requirement of the vibrational mode of a molecule to be Raman active?

(h) What is the photoelectric effect? Write the equation of Einstein's photoelectric law.

1. Explain the origin of atomic spectrum:

The atomic spectrum originates from the transitions of electrons between discrete energy levels or orbitals within an atom. When atoms are exposed to energy (like heat or electromagnetic radiation), their electrons are excited to higher energy levels. However, these excited electrons eventually return to their ground state (the lowest energy state), and in doing so, they release energy in the form of light.

2. What is meant by anisotropy of chemical bond? Give an example:

Anisotropy in chemical bonding refers to the directional dependence of the properties of a bond. In simpler terms, it means that the strength and nature of a chemical bond may vary depending on the direction in which it is measured. This behavior is especially evident in covalent bonds, where electron density is not uniformly distributed along all axes.

3. What makes TMS a molecule of choice to act as a reference in NMR spectroscopy?

TMS (Tetramethylsilane, $Si(CH_3)_4$) is the preferred reference molecule in nuclear magnetic resonance (NMR) spectroscopy due to its several favorable properties:

- **Inertness**: TMS is chemically stable and does not interact with the sample, making it ideal for use in a variety of solvents.

- **Simplicity**: TMS has a single peak in the proton NMR spectrum, typically at 0 ppm, which makes it easy to identify.

4. What is meant by polarizability of a molecule?

Polarizability refers to the ability of a molecule to form an induced dipole moment in the presence of an external electric field. It is a measure of how easily the electron cloud around a molecule can be distorted by an external force. Larger and more electronegative atoms tend to be more polarizable, as their electron clouds are more easily shifted.

5. In what way is NMR spectrometry different from other molecular spectroscopic methods?

NMR (Nuclear Magnetic Resonance) spectroscopy differs from other molecular spectroscopic techniques in its ability to provide detailed information about the molecular structure through interactions between nuclear spins and an applied magnetic field.

Key differences include:

- **Nuclear Information**: NMR focuses on the magnetic properties of nuclei (like hydrogen or carbon), unlike IR (infrared) spectroscopy, which probes vibrational modes of molecules.
- **Quantitative and Qualitative Analysis**: NMR provides both qualitative (structure identification) and quantitative (concentration analysis) data, which is not typically achievable with techniques like UV-Vis.

6. What is the importance of 13C-NMR spectroscopy in structure determination?

13C-NMR spectroscopy is vital in structure determination, particularly in organic chemistry, because it provides detailed information about the carbon framework of a molecule. Carbon-13 nuclei are naturally found in trace amounts in most organic compounds (approximately 1% of all carbon atoms), but they have a magnetic moment that allows them to interact with an applied magnetic field in NMR spectroscopy.

13C-NMR helps in identifying:

- **Types of Carbon Environments**: It can differentiate between different carbon atoms (e.g., quaternary, methyl, and carbonyl groups).
- **Connectivity**: 13C-NMR can show how carbon atoms are connected to each other, which is crucial for determining the overall structure of a compound.
- **Isotopic Information**: The natural abundance of 13C allows for the identification of specific carbon atoms in a molecule without interference from the more abundant 12C isotope.

7. What is the requirement of the vibrational mode of a molecule to be Raman active?

For a molecule to be Raman active, it must undergo a change in polarizability during vibration. Raman spectroscopy is based on the inelastic scattering of light, where the energy of the scattered photon is shifted due to the interaction with the vibrational modes of a molecule. If the vibration of the molecule induces a fluctuation in the electron density (polarizability), the vibration will interact with the incident light, and a Raman shift will occur.

8. What is the photoelectric effect? Write the equation of Einstein's photoelectric law.

The photoelectric effect refers to the phenomenon where electrons are ejected from the surface of a material when it is exposed to light (usually ultraviolet). The energy of the incoming photons is transferred to electrons in the material, causing them to overcome the work function (the minimum energy needed to eject an electron) and be emitted from the surface.

Einstein's photoelectric equation is given as:

$$E_k = hf - \phi$$

- Ek = Kinetic energy of the emitted electron
- h = Planck's constant
- f = Frequency of the incident light
- ϕ = Work function (the minimum energy required to eject an electron from the material)

2. (a) (i) 5G services in India are provided at a frequency of 3300 MHz. Calculate the wavelength of the radiation.

(ii) Explain why the atomic spectra are line spectra whereas the molecular spectra are band spectra.

(b) A photon of visible light has a wavelength of 550 nm. Calculate its

(i) wavenumber

(ii) frequency

(iii) energy per mol

(a) (i) Calculate the wavelength of the radiation for 5G services in India:

The frequency (f) of the radiation for 5G services in India is 3300 MHz, which is 3.3×10^9 Hz. To calculate the wavelength (λ\lambdaλ) of the radiation, we can use the formula:

$$\lambda = \frac{c}{f}$$

Where:

- c = speed of light in vacuum = 3×10^8 m/s
- f = frequency of the radiation = 3300 MHz = 3.3×10^9 Hz

Substitute the values into the equation:

$$\lambda = \frac{3 \times 10^8 \, \text{m/s}}{3.3 \times 10^9 \, \text{Hz}} = 0.0909 \, \text{m}$$

Thus, the wavelength of the radiation is approximately **0.0909 meters** or **9.09 cm**.

(ii) Explain why atomic spectra are line spectra, whereas molecular spectra are band spectra:

The distinction between atomic and molecular spectra lies in the different types of energy transitions involved:

- **Atomic Spectra (Line Spectra):**Atomic spectra consist of discrete lines because the energy levels in atoms are quantized. When an atom absorbs or emits energy, its electrons transition between specific, discrete energy levels. These transitions correspond to specific wavelengths of light, producing sharp lines in the spectrum. Since atoms have a single nucleus and relatively fewer electrons compared to molecules, their energy levels are spaced further apart, leading to distinct and narrow lines.
- **Molecular Spectra (Band Spectra):**Molecular spectra are broader and consist of bands because molecules have more complex energy states. These include not only electronic energy levels, like atoms, but also vibrational and rotational energy levels. As a result, when a molecule absorbs or emits radiation, multiple transitions occur simultaneously across different vibrational and rotational levels, leading to the formation of bands rather than individual lines. The interactions between these energy levels lead to a more complex structure in the spectrum, producing bands instead of sharp lines.

(b) A photon of visible light has a wavelength of 550 nm. Calculate its:

Given:

- Wavelength $\lambda = 550 \, \text{nm} = 550 \times 10^{-9} \, \text{m}$
- Speed of light $c = 3 \times 10^8 \, \text{m/s}$
- Planck's constant $h = 6.626 \times 10^{-34} \, \text{J\cdotps}$

(i) Wavenumber (ν~):

Wavenumber is the reciprocal of the wavelength, usually expressed in cm^{-1}. It is given by:

$$\tilde{\nu} = \frac{1}{\lambda}$$

To convert the wavelength from meters to centimeters:

$$\lambda = 550 \times 10^{-9}\,\text{m} = 5.5 \times 10^{-7}\,\text{m} = 5.5 \times 10^{-5}\,\text{cm}$$

Now calculate th

$$\tilde{\nu} = \frac{1}{5.5 \times 10^{-5}} = 1.818 \times 10^{4}\,\text{cm}^{-1}$$

Thus, the **wavenumber** is approximately **1.818×10^4 cm^{-1}**.

(ii) Frequency (ν):

The frequency ν\nuν of the photon can be calculated using the relation:

$$\nu = \frac{c}{\lambda}$$

Substitute the known values:

$$\nu = \frac{3 \times 10^{8}\,\text{m/s}}{550 \times 10^{-9}\,\text{m}} = 5.455 \times 10^{14}\,\text{Hz}$$

Thus, the **frequency** is approximately **5.455×10^{14} Hz**.

(iii) Energy per mol:

To calculate the energy per mole of photons, we first need to find the energy of a single photon. The energy of a photon is given by:

$$E = h\nu$$

Substitute the values:

$$E = (6.626 \times 10^{-34}\,\text{J\cdotps}) \times (5.455 \times 10^{14}\,\text{Hz}) = 3.615 \times 10^{-19}\,\text{J}$$

This is the energy for one photon. Now, to find the energy for one mole of photons, multiply by Avogadro's number $(N_A = 6.022 \times 10^{23})$:

$$E_{\text{mol}} = (3.615 \times 10^{-19}\,\text{J}) \times (6.022 \times 10^{23}) = 2.18 \times 10^{5}\,\text{J/mol}$$

Thus, the **energy per mole** of photons is approximately **2.18×10^5 J/mol**.

3. (a) What is meant by the Balmer series of hydrogen? What will be the wave number of the longest wavelength in the Balmer series?

(b) A photoelectron spectrum of a compound containing nitrogen (N), aluminium (Al), and fluorine (F) shows three strong peaks at the following binding energies:

• Peak X: ~686 eV

• Peak Y: ~399 eV

• Peak Z: ~73 eV

Find the best option from the choices given below that best explains the relative positioning of these peaks in terms of binding energy.

(i) Peak X corresponds to F 1s electrons, which have the highest binding energy because fluorine's high electronegativity and small size give its 1s electrons a large effective nuclear attraction. Peak Y is N 1s and Peak Z is Al 2p.

(ii) Nitrogen has more valence electrons than fluorine or aluminium, therefore its peak appears at the highest binding energy.

(iii) The spectrum shows more aluminium atoms than nitrogen or fluorine, so its peak appears at the lowest binding energy due to dilution.

(iv) Aluminium has the highest nuclear charge, so its 2p peak should have the largest binding energy, but shielding effects reverse this trend. Justify your answer.

(a) What is meant by the Balmer series of hydrogen?

The **Balmer series** is a set of spectral lines of the hydrogen atom that result from electronic transitions of the electron from higher energy levels to the second energy level (n = 2) of the

hydrogen atom. When an electron in a hydrogen atom absorbs energy, it can move to a higher energy level (excited state). As the electron returns to the second energy level, energy is released in the form of light. These emitted light waves correspond to specific wavelengths, which form the Balmer series.

The general formula for the wavelengths of the Balmer series is given by the **Rydberg formula**:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

Where:

- λ is the wavelength of the emitted light
- RH is the Rydberg constant for hydrogen (RH=1.097×107 m−1)
- nnn is the principal quantum number of the higher energy level, where n≥3

The Balmer series specifically corresponds to transitions from higher energy levels (n = 3, 4, 5, ...) to the second energy level (n = 2). The lines of the Balmer series lie in the visible spectrum.

What will be the wave number of the longest wavelength in the Balmer series?

The longest wavelength in the Balmer series corresponds to the transition from the **n = 3** to **n = 2** energy level (the smallest energy transition within the series). Using the **Rydberg formula** for the wave number, we can calculate the wave number for this transition.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

Substitute the values:

$$\frac{1}{\lambda} = (1.097 \times 10^7) \left(\frac{1}{4} - \frac{1}{9} \right)$$

First, calculate the difference:

$$\frac{1}{4} - \frac{1}{9} = \frac{9 - 4}{36} = \frac{5}{36}$$

Now, substitute this into the equation:

$$\frac{1}{\lambda} = (1.097 \times 10^7) \times \frac{5}{36} = 1.524 \times 10^6 \, \text{m}^{-1}$$

Thus, the wave number ν~ of the longest wavelength in the Balmer series is approximately **1.524×10^6 m^{-1}**.

(b) Photoelectron Spectrum Analysis:

The given photoelectron spectrum shows three strong peaks at the following binding energies:

- **Peak X**: ~686 eV
- **Peak Y**: ~399 eV
- **Peak Z**: ~73 eV

We need to identify which of the provided explanations best fits these observed binding energies for nitrogen (N), aluminum (Al), and fluorine (F).

Understanding the Binding Energies:

Binding energy in a photoelectron spectrum represents the energy required to remove an electron from a specific shell or orbital in an atom. Higher binding energy corresponds to electrons being in deeper, more tightly bound orbitals, such as the 1s orbital. Lower binding energy corresponds to electrons in orbitals that are more loosely bound, such as 2p or 2s orbitals.

Analysis of Each Peak:

1. **Peak X: ~686 eV**
    - The highest binding energy is typically associated with the 1s orbital of an atom. Among the three elements (N, Al, and F), **fluorine** has the smallest atomic radius and the highest electronegativity, which leads to a greater nuclear attraction on its electrons, particularly in the 1s orbital. As a result, the binding energy for fluorine's 1s electrons will be the highest.
2. **Peak Y: ~399 eV**
    - **Nitrogen** has a relatively high nuclear charge and electronegativity, but its electrons in the 1s orbital are not as tightly bound as those of fluorine due to its larger size and less effective nuclear charge. This suggests that the peak at **399 eV** most likely corresponds to nitrogen's 1s orbital electrons. This binding energy

is lower than that of fluorine, which is expected due to fluorine's stronger nuclear attraction.

3. **Peak Z: ~73 eV**
    - This binding energy is typical of electrons from a **2p** orbital, which are more loosely bound than 1s electrons. Among the three elements, **aluminum** is likely to have the 2p orbital electron with this binding energy. Aluminum is a metal with a relatively low ionization energy compared to nitrogen and fluorine, so its 2p electrons are more loosely bound, resulting in a lower binding energy.

Interpretation of Options:

- **(i) Peak X corresponds to F 1s electrons, which have the highest binding energy because fluorine's high electronegativity and small size give its 1s electrons a large effective nuclear attraction. Peak Y is N 1s and Peak Z is Al 2p.**
    - This option is **correct**. Fluorine has the highest binding energy for its 1s electrons, followed by nitrogen's 1s, and then aluminum's 2p.
- **(ii) Nitrogen has more valence electrons than fluorine or aluminium, therefore its peak appears at the highest binding energy.**
    - This is **incorrect** because the number of valence electrons does not directly correlate with binding energy. Binding energy is more influenced by nuclear charge and electron shielding, not just the number of valence electrons.
- **(iii) The spectrum shows more aluminium atoms than nitrogen or fluorine, so its peak appears at the lowest binding energy due to dilution.**
    - This option is **incorrect** because dilution does not affect binding energy. The binding energy depends on the nuclear charge and the electron's position in the atom, not on the concentration of the element in the sample.
- **(iv) Aluminium has the highest nuclear charge, so its 2p peak should have the largest binding energy, but shielding effects reverse this trend.**
    - This is **incorrect**. Although aluminum has a higher nuclear charge than nitrogen and fluorine, its 2p electrons are more shielded, leading to a lower binding energy compared to fluorine's 1s electrons.

4. (a) (i) What information about the molecule can be obtained from a rotation spectrum?

(ii) What is meant by a selection rule? Give the selection rule for a rotating diatomic molecule modelled as a rigid rotator.

(b) Assuming that the force constants of H-Cl and D-Cl are the same, calculate the fundamental vibration frequency of D-Cl if that of H-Cl is 2890 cm-1.

(a) (i) What information about the molecule can be obtained from a rotation spectrum?

A **rotation spectrum** provides valuable information about the rotational transitions of a molecule. These transitions are due to changes in the rotational energy levels of the molecule, and the spectrum gives insights into several key characteristics of the molecule, including:

1. **Bond Length and Moment of Inertia**:The rotational spectrum can be used to calculate the molecule's **moment of inertia (I)**, which is related to the distribution of mass in the molecule. The moment of inertia for a diatomic molecule is given by the formula:

$$I = \mu r^2$$

Where:

- μ is the reduced mass of the molecule, $\mu = \frac{m_1 m_2}{m_1 + m_2}$
- r is the bond length (distance between the two nuclei).

By analyzing the rotational spectrum, the bond length of the molecule can be determined, as it influences the moment of inertia.

2. **Rotational Energy Levels**:The energy associated with the rotational motion of the molecule is quantized, and the spectrum provides data on the energy difference between these levels. The rotational energy levels of a rigid diatomic molecule are given by:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

Where:

- J is the rotational quantum number.
- h is Planck's constant.
- I is the moment of inertia.
- J(J+1) represents the rotational energy level.

From the spectrum, the spacing between rotational levels can be used to determine the molecular properties, such as the **moment of inertia**, which in turn can reveal the structure of the molecule.

3. **Types of Molecules**:The rotational spectrum can help identify whether a molecule is **linear** or **non-linear**. Linear molecules have different rotational spectra compared to non-linear molecules due to their different symmetry properties.
4. **Isotopic Substitution Effects**:When a molecule undergoes isotopic substitution (e.g., replacing hydrogen with deuterium), the change in mass affects the rotational spectrum. The rotational constant changes as the moment of inertia changes with isotopic substitution, and this can be observed in the spectrum.

(ii) What is meant by a selection rule? Give the selection rule for a rotating diatomic molecule modeled as a rigid rotator.

A **selection rule** in spectroscopy is a guideline that determines the allowed transitions between energy levels of a molecule based on certain quantum mechanical principles. It dictates which transitions can or cannot occur when the molecule absorbs or emits electromagnetic radiation.

For rotational spectra, the **selection rule** governs the allowed transitions between rotational energy levels of a molecule.

For a **rigid rotator** model (such as a diatomic molecule rotating in space), the selection rule for rotational transitions is:

$$\Delta J = \pm 1$$

Where:

- J is the rotational quantum number.

This means that for a molecule to absorb or emit radiation and undergo a rotational transition, the initial and final rotational quantum numbers must differ by 1. That is, a transition from $J = 0$ to $J = 1$ or from $J = 1$ to $J = 2$, and so on, is allowed. However, transitions such as $J = 0$ to $J = 2$ or $J = 1$ to $J = 3$ are not allowed by the selection rule.

This rule arises because:

- The molecule can absorb or emit a photon that causes a change in angular momentum.
- The angular momentum of the photon corresponds to the change in the rotational quantum number, and the allowed change in J is limited to ±1 due to the nature of angular momentum in quantum mechanics.

(b) Assuming that the force constants of H-Cl and D-Cl are the same, calculate the fundamental vibration frequency of D-Cl if that of H-Cl is 2890 cm^{-1}.

The fundamental vibration frequency of a diatomic molecule is given by:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Where:

- ν is the frequency of vibration.
- k is the force constant (assumed to be the same for H-Cl and D-Cl).
- μ is the reduced mass of the molecule.

The reduced mass μ is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

For H-Cl, where:

- The mass of hydrogen, mH=1 amu.
- The mass of chlorine, mCl=35.5 amu.

The reduced mass of H-Cl is:

$$\mu_{\text{H-Cl}} = \frac{1 \times 35.5}{1 + 35.5} = \frac{35.5}{36.5} = 0.972\,\text{amu}$$

For D-Cl, where:

- The mass of deuterium, mD=2 amu.
- The mass of chlorine remains the same, mCl=35.5 amu.

The reduced mass of D-Cl is:

$$\mu_{\text{D-Cl}} = \frac{2 \times 35.5}{2 + 35.5} = \frac{71}{37.5} = 1.893\,\text{amu}$$

The vibration frequency is inversely proportional to the square root of the reduced mass. The ratio of the frequencies for D-Cl and H-Cl is:

$$\frac{\nu_{\text{D-Cl}}}{\nu_{\text{H-Cl}}} = \sqrt{\frac{\mu_{\text{H-Cl}}}{\mu_{\text{D-Cl}}}}$$

Substitute the values of the reduced masses:

$$\frac{\nu_{\text{D-Cl}}}{\nu_{\text{H-Cl}}} = \sqrt{\frac{0.972}{1.893}} = \sqrt{0.513} = 0.715$$

Thus, the vibration frequency of D-Cl is:

$$\nu_{\text{D-Cl}} = 0.715 \times \nu_{\text{H-Cl}} = 0.715 \times 2890\,\text{cm}^{-1}$$

$$\nu_{\text{D-Cl}} \approx 2062\,\text{cm}^{-1}$$

Therefore, the **fundamental vibration frequency of D-Cl** is approximately **2062 cm⁻¹**.

5. (a) In Raman spectra, the Stokes line are more intense than the anti-Stokes lines. Why?

(b) The rotational Raman spectrum of a diatomic molecule has the first line of a series of Stokes and anti-Stokes lines at 346 cm-1, relative of the ν would be its bond length. of incident light. What

(c) CN+ has bond length 129 pm. Calculate the wavenumbers of the first four lines in its microwave spectrum.

[Given: mass of C=12.000 u and mass of N=14.007 u]

(a) Why are Stokes lines more intense than anti-Stokes lines in Raman spectra?

In **Raman spectroscopy**, the observed scattering of light is classified into **Stokes** and **anti-Stokes** lines based on the energy of the scattered photons relative to the incident photons.

- **Stokes Lines**: These occur when the scattered photon has **lower energy** than the incident photon, meaning the molecule absorbs some of the photon's energy and

undergoes a transition to a higher vibrational energy state. The molecule is in a lower energy state before the scattering event, and after scattering, it is in a higher vibrational state.

- **Anti-Stokes Lines**: These occur when the scattered photon has **higher energy** than the incident photon, meaning the molecule transfers some of its energy to the scattered photon and undergoes a transition to a lower vibrational energy state. The molecule must initially be in a higher energy state for this to happen.

Why are Stokes lines more intense?The relative intensities of Stokes and anti-Stokes lines are primarily determined by the population distribution of molecules in various vibrational energy states according to **Boltzmann distribution**. At room temperature, most molecules are in the **ground vibrational state (lowest energy state)**. This means there are far more molecules available to undergo **Stokes scattering**, where the molecule is excited from the ground state to a higher vibrational state, than to undergo **anti-Stokes scattering**, which requires the molecule to already be in an excited state.

Since the population of molecules in higher vibrational states is much smaller (as dictated by the Boltzmann distribution), **anti-Stokes lines** are much weaker than **Stokes lines** because fewer molecules are available to undergo this process. Additionally, the Stokes process is favored because it involves a larger number of molecules in the ground vibrational state compared to those in excited states.

Therefore, **Stokes lines are more intense than anti-Stokes lines** due to the higher population of molecules in the ground vibrational state and the distribution of molecular energy levels according to temperature.

(b) The rotational Raman spectrum of a diatomic molecule has the first line of a series of Stokes and anti-Stokes lines at 346 cm^{-1}. Calculate the bond length of the molecule.

The **Raman rotational spectrum** involves the transitions between rotational energy levels. The spacing between the lines in the rotational Raman spectrum is given by:

$$\Delta\tilde{\nu} = 4B$$

Where:

- $\Delta\nu\sim$ is the spacing between the lines (in cm^{-1}),
- B is the rotational constant of the molecule (in cm^{-1}).

In this case, the first line in the series is at **346 cm^{-1}**, which represents the spacing between the lines. Hence, the rotational constant B can be determined from:

$$B = \frac{346}{4} = 86.5\,\text{cm}^{-1}$$

The rotational constant B is related to the bond length rrr (the distance between the two atoms in the diatomic molecule) by the equation:

$$B = \frac{h}{8\pi^2 I c}$$

Where:

- h is Planck's constant ($6.626 \times 10^{-34}\,\mathrm{J\cdot s}$),
- I is the moment of inertia of the molecule,
- c is the speed of light ($3.0 \times 10^8\,\mathrm{m/s}$).

The moment of inertia I for a diatomic molecule is given by:

$$I = \mu r^2$$

Where μ is the reduced mass of the molecule, defined as:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

For a diatomic molecule, m1 and m2 are the masses of the two atoms. Let's assume the molecule is made of two atoms with atomic masses m1=m2, and we'll convert the reduced mass into kg.

Let m1 and m2 be in atomic mass units (u), and for a diatomic molecule, we use the atomic masses of the atoms.

(c) Calculate the wavenumbers of the first four lines in the microwave spectrum of CN^+.

Given:

- The bond length of CN^+ is **129 pm** (which is $129 \times 10^{-12}\,\mathrm{m}$),
- The atomic masses of **C** and **N** are $m_C = 12.000\,\mathrm{u}$ and $m_N = 14.007\,\mathrm{u}$,
- The force constant is given as $k = 9.67\,\mathrm{m}^{-1}$ (force constant for CN).

We use the following relationships to find the wavenumbers of the first four lines in the microwave spectrum:

1. **Reduced mass** for CN:

$$\mu = \frac{m_C \times m_N}{m_C + m_N} = \frac{12 \times 14.007}{12 + 14.007} = \frac{168.084}{26.007} = 6.46\,\mathrm{u}$$

To convert this into kg, multiply by 1.66×10−27:

$$\mu = 6.46\,\mathrm{u} \times 1.66 \times 10^{-27}\,\mathrm{kg/u} = 1.07 \times 10^{-26}\,\mathrm{kg}$$

2. **Bond length** of CN:

$$r = 129\,\mathrm{pm} = 129 \times 10^{-12}\,\mathrm{m}$$

3. **Moment of inertia**:

$$I = \mu r^2 = 1.07 \times 10^{-26} \times (129 \times 10^{-12})^2 = 1.77 \times 10^{-46}\,\mathrm{kg\cdotpm^2}$$

4. **Rotational constant B**:

$$B = \frac{h}{8\pi^2 I c}$$

Where:

- $h = 6.626 \times 10^{-34}\,\mathrm{J\cdotps}$,
- $c = 3.0 \times 10^{8}\,\mathrm{m/s}$,
- $I = 1.77 \times 10^{-46}\,\mathrm{kg\cdotpm^2}$.

Substituting into the equation:

$$B = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 1.77 \times 10^{-46} \times 3.0 \times 10^{8}}$$

$$B = 2.39 \times 10^{10}\,\mathrm{Hz}$$

Now, to convert the frequency into wavenumbers, use:

$$\tilde{\nu} = \frac{B}{c} = \frac{2.39 \times 10^{10}}{3.0 \times 10^{8}} = 79.67\,\text{cm}^{-1}$$

So, the **rotational constant** for CN^+ is approximately **79.67 cm^{-1}**.

Now, for the **first four lines** of the microwave spectrum, the wavenumbers of the lines will be:

- $J = 1 \rightarrow J = 0$ (first line): $\tilde{\nu}_1 = 79.67\,\text{cm}^{-1}$,
- $J = 2 \rightarrow J = 1$ (second line): $\tilde{\nu}_2 = 2 \times 79.67 = 159.34\,\text{cm}^{-1}$,
- $J = 3 \rightarrow J = 2$ (third line): $\tilde{\nu}_3 = 3 \times 79.67 = 239.01\,\text{cm}^{-1}$,
- $J = 4 \rightarrow J = 3$ (fourth line): $\tilde{\nu}_4 = 4 \times 79.67 = 319.68\,\text{cm}^{-1}$.

Thus, the **wavenumbers of the first four lines** in the microwave spectrum of CN^+ are:

- 79.67 cm^{-1},
- 159.34 cm^{-1},
- 239.01 cm^{-1},
- 319.68 cm^{-1}.

6. (a) (i) Calculate the number of vibrational modes for a molecule of methane.

(ii) The frequencies of the first and second overtones respectively are exactly double and triple of the fundamental vibration frequency. Comment.

(b) Raman rotational spectra of H2 was observed with Hg light with Rayleigh line at 2294 cm-1. Stokes lines were observed at 22581, 22337, 22094, 21851 cm-1. Draw the rotational energy level diagram with Stokes and anti Stokes lines.

(a) (i) Calculate the number of vibrational modes for a molecule of methane (CH_4):

A **vibrational mode** refers to the independent way in which the atoms of a molecule can move relative to one another while maintaining the overall structure. The number of vibrational modes in a molecule is determined by the number of atoms and the degrees of freedom available for motion.

For a **non-linear molecule** like methane (CH_4), the number of vibrational modes can be calculated using the following formula:

$$\text{Number of vibrational modes} = 3N - 6$$

Where:

- N is the number of atoms in the molecule.

Methane (CH_4) consists of **5 atoms** (1 carbon and 4 hydrogen atoms), so:

$$\text{Number of vibrational modes} = 3(5) - 6 = 15 - 6 = 9$$

Therefore, **methane has 9 vibrational modes**.

Out of these 9 modes:

- 3 modes correspond to **translational motion** (motion of the entire molecule).
- 3 modes correspond to **rotational motion** (rotation of the molecule).
- The remaining **3 modes** are **vibrational modes**.

Thus, **methane has 9 vibrational modes**, including both stretching and bending modes.

(ii) The frequencies of the first and second overtones respectively are exactly double and triple of the fundamental vibration frequency. Comment.

In molecular vibration spectroscopy, the **fundamental frequency** is the frequency at which the molecule vibrates in its lowest energy state (ground state). **Overtones** refer to higher-energy vibrational transitions where the molecule vibrates at integer multiples of the fundamental frequency.

- **First overtone**: This occurs when the molecule is in the second vibrational state (first excited state) and the frequency is **approximately twice the fundamental frequency**.
- **Second overtone**: This occurs when the molecule is in the third vibrational state (second excited state) and the frequency is **approximately three times the fundamental frequency**.

For most **harmonic oscillators**, the overtone frequencies are exact integer multiples of the fundamental frequency (i.e., **2ν, 3ν**), where ν is the fundamental frequency. However, real molecules exhibit **anharmonicity**, meaning that the relationship between the overtone frequencies and the fundamental frequency is not exactly linear, and overtones are usually not perfect multiples of the fundamental.

The **perfect doubling (2v) and tripling (3v)** of the fundamental vibration frequency observed in this case suggests that the molecule may be approximated as a **harmonic oscillator** within the low-energy region. In reality, overtone intensities decrease with higher overtones, and the energy gap between vibrational states becomes less uniform as the molecule moves higher in energy.

(b) Raman rotational spectra of H_2 were observed with Hg light with the Rayleigh line at 2294 cm^{-1}. Stokes lines were observed at 22581, 22337, 22094, and 21851 cm^{-1}. Draw the rotational energy level diagram with Stokes and anti-Stokes lines.

To analyze the Raman rotational spectra of H_2 and draw the rotational energy level diagram, we need to understand the relationship between the observed frequencies (Stokes lines) and the rotational energy levels of H_2.

Given:

- **Rayleigh line** at 2294 cm^{-1},
- Stokes lines observed at **22581 cm^{-1}, 22337 cm^{-1}, 22094 cm^{-1}, and 21851 cm^{-1}**.

The difference between the **Rayleigh line** (which corresponds to no energy exchange) and the Stokes lines corresponds to the energy required for a rotational transition.

Step 1: Determine the energy gap between consecutive Stokes lines.

The **Rayleigh line** is the central, unshifted frequency, corresponding to the molecule in its initial state (no transition). The **Stokes lines** represent the molecule's transition from a lower rotational energy level to a higher one. The differences between the successive Stokes lines are as follows:

- $22581 - 22337 = 244\,\mathrm{cm}^{-1}$
- $22337 - 22094 = 243\,\mathrm{cm}^{-1}$
- $22094 - 21851 = 243\,\mathrm{cm}^{-1}$

The approximate spacing between the lines is consistent at **243 cm^{-1}**.

Step 2: The rotational energy levels.

For a diatomic molecule like H_2, the rotational energy levels are quantized and follow the equation:

$$E_J = BJ(J+1)$$

Where:

- EJ is the energy of the J-th rotational level,

- B is the rotational constant,
- J is the rotational quantum number.

Step 3: Relate the energy gap to the rotational constant BBB.

The **spacing between rotational levels** in a Raman spectrum is related to the rotational constant B by:

$$\Delta E = 2B$$

From the observed differences between the Stokes lines, we approximate:

$$\Delta E = 244\,\text{cm}^{-1}$$

This is the energy difference between two adjacent rotational levels. Since this corresponds to **2B**, we calculate:

$$B = \frac{244}{2} = 122\,\text{cm}^{-1}$$

Step 4: Energy level diagram.

Now that we have the rotational constant $B = 122\,\text{cm}^{-1}$, we can draw the **rotational energy levels** for H_2. These energy levels are separated by $2B = 244\,\text{cm}^{-1}$.

For H_2, the energy levels are quantized as:

- $J = 0 \rightarrow$ **ground state** (Rayleigh line),
- $J = 1 \rightarrow$ first excited state,
- $J = 2 \rightarrow$ second excited state,
- $J = 3 \rightarrow$ third excited state, and so on.

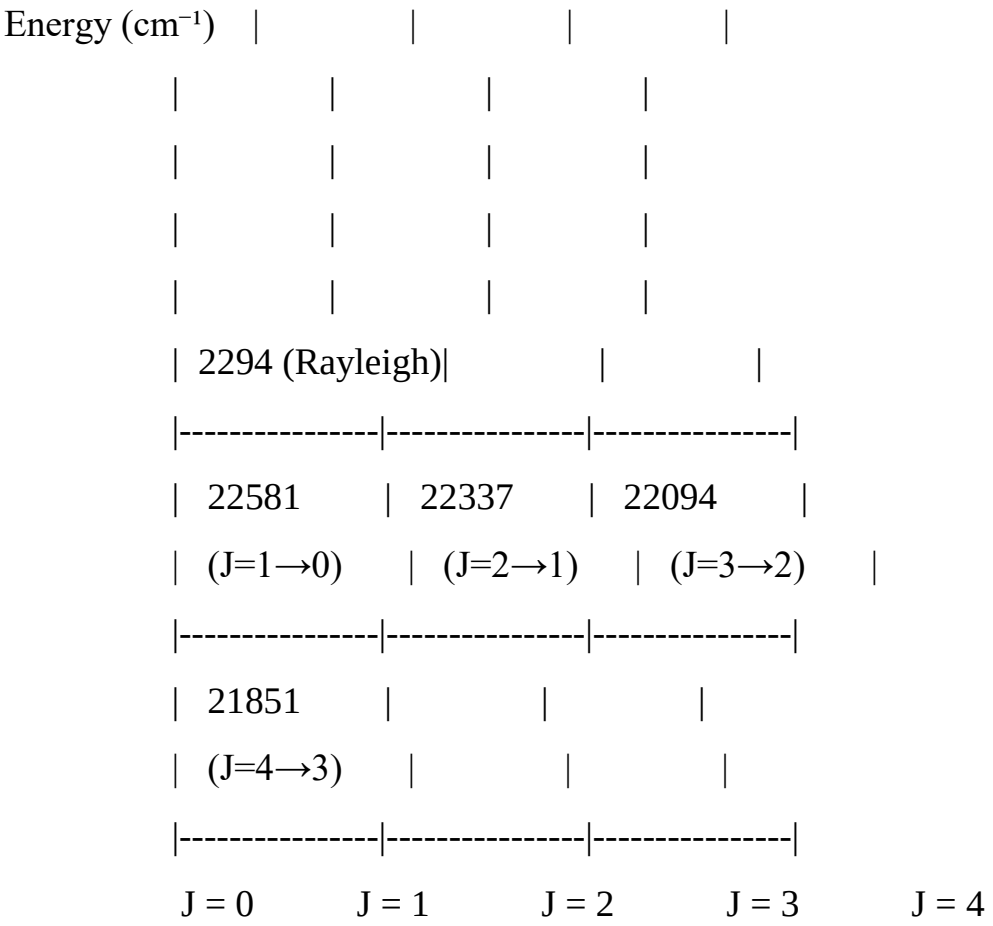
The energy of each rotational level is given by:

$$E_J = 122J(J+1)\,\text{cm}^{-1}$$

Now, to illustrate the **Raman spectrum**, let's focus on the **Stokes lines**:

- The **Rayleigh line** corresponds to the $J = 0$ state (no transition).
- The first **Stokes line** at 22581 cm^{-1} corresponds to the $J = 1 \rightarrow J = 0$ transition.
- The second **Stokes line** at 22337 cm^{-1} corresponds to the $J = 2 \rightarrow J = 1$ transition.
- The third **Stokes line** at 22094 cm^{-1} corresponds to the $J = 3 \rightarrow J = 2$ transition.
- The fourth **Stokes line** at 21851 cm^{-1} corresponds to the $J = 4 \rightarrow J = 3$ transition.

Rotational Energy Level Diagram:



- The **Rayleigh line** (2294 cm^{-1}) is the unshifted line corresponding to no energy transfer.
- The **Stokes lines** appear as the molecule absorbs energy and transitions to higher rotational levels.

7. (a) (i) Electronic transitions are called vertical transitions. Comment.

(ii) A light source of wavelength λ illuminates a metal surface and electron are ejected with the maximum kinetic energy 2 eV. If the same surface is illuminated by a light source of wavelength $\lambda/3$, then calculate the maximum kinetic energy of the ejected electron. (Work function of metal is 1 eV)

(b) (i) How does the rule of Mutual Exclusion help in predicting the symmetry in case of H2O and CO2 molecules?

(ii) The molecule X2Y has 3 fundamental vibrational frequencies. One is Raman active and two are IR active. Identify the structure of the molecule.

(a) (i) Electronic transitions are called vertical transitions. Comment.

Electronic transitions are often referred to as **vertical transitions** because the energy change during the transition is primarily associated with the movement of electrons between discrete electronic energy levels. This term "vertical" comes from the way these transitions are represented in a **potential energy diagram**.

- In such diagrams, the **electronic energy levels** are represented as horizontal lines, and transitions between these levels occur without any significant change in the nuclear positions. This means that the **nuclei** of the atoms or molecules remain in the same position during the transition, and the electron moves from one electronic energy level to another.
- These transitions are termed "vertical" because the electron jumps from one energy level to another in a **direct manner** (vertically in the diagram) without the need for an intermediate step involving a change in nuclear positions (i.e., the electron is excited instantly to a higher energy level).

In **molecular systems**, the term **vertical transition** is used because the electron's transition typically occurs between energy levels that are relatively close together in terms of nuclear vibration, leading to minimal displacement of nuclei during the transition. This is why **Franck-Condon principle** applies, which describes that **vertical transitions** are favored when the nuclear positions do not change significantly during the electronic transition.

(ii) A light source of wavelength λ illuminates a metal surface, and electrons are ejected with the maximum kinetic energy of 2 eV. If the same surface is illuminated by a light source of wavelength $\lambda/3$, then calculate the maximum kinetic energy of the ejected electron. (Work function of metal is 1 eV)

To solve this, we will use the **photoelectric equation**, which is given by:

$$K.E. = h\nu - \phi$$

Where:

- $K.E.$ is the kinetic energy of the ejected electron,
- h is Planck's constant ($6.626 \times 10^{-34}\,\mathrm{J\cdot s}$),
- ν is the frequency of the incident light,
- ϕ is the work function of the metal.

The frequency ν\nuν is related to the wavelength λ\lambdaλ by the equation:

$$\nu = \frac{c}{\lambda}$$

Where:

- c is the speed of light (3.0×108 m/s),
- λ is the wavelength of the incident light.

We know:

- The work function ϕ of the metal is **1 eV**,
- The maximum kinetic energy for wavelength λ.

First, let's calculate the kinetic energy for the original wavelength λ:

$$K.E = h\nu - \phi$$

$$2\,\mathrm{eV} = h\left(\frac{c}{\lambda}\right) - 1\,\mathrm{eV}$$

$$h\left(\frac{c}{\lambda}\right) = 3\,\mathrm{eV}$$

Now, for the second light source with wavelength λ/3\lambda/3λ/3, the frequency will be **3 times higher**, i.e., ν′=3ν.

The energy of the ejected electron is now:

$$K.E' = h\nu' - \phi$$

$$K.E' = h(3\nu) - 1\,\mathrm{eV}$$

$$K.E' = 3 \cdot h\nu - 1\,\mathrm{eV}$$

Since we already know hν=3 eV:

$$K.E' = 3 \cdot 3\,\text{eV} - 1\,\text{eV}$$

$$K.E' = 9\,\text{eV} - 1\,\text{eV}$$

$$K.E' = 8\,\text{eV}$$

Therefore, the maximum kinetic energy of the ejected electron for the light with wavelength λ/3.

(b) (i) How does the rule of Mutual Exclusion help in predicting the symmetry in the case of H_2O and CO_2 molecules?

The **Mutual Exclusion Principle** is a rule used in **group theory** to predict the symmetry properties of molecular vibrations. It helps in determining which vibrational modes are **IR active** (active in Infrared spectroscopy) and which are **Raman active** (active in Raman spectroscopy).

According to this principle:

- **In a molecule, the symmetry of a vibration must be different for Raman and IR activity**.
- If a vibration mode is **IR active**, it will be **Raman inactive**, and if it is **Raman active**, it will be **IR inactive**.

Let's apply the **Mutual Exclusion Principle** to the **H_2O** and **CO_2** molecules:

H_2O Molecule:

- **Symmetry of H_2O**: The H_2O molecule has a **bent geometry**, which belongs to the **C_{2v}** point group. This point group has symmetry elements like the identity, two vertical mirrors, and a 2-fold rotation axis.
- **IR Active Modes**: In the case of H_2O, the molecule has an **A_1** symmetry mode corresponding to the **symmetric stretch**, which is **IR active** because it involves a change in dipole moment.
- **Raman Active Modes**: The **B_1** and **B_2** modes are **Raman active** because they correspond to bending motions that induce a change in polarizability.
- **Mutual Exclusion**: The **A_1** mode is IR active but Raman inactive, while the **B_1** and **B_2** modes are Raman active but IR inactive, which is in line with the **Mutual Exclusion Principle**.

CO_2 Molecule:

- **Symmetry of CO_2**: CO_2 is a **linear** molecule belonging to the **D_2h** point group. It has symmetry elements such as the identity, 2-fold rotation axis, and mirror planes.
- **IR Active Modes**: In CO_2, the **symmetric stretching** vibration (mode ν1\nu_1ν1) is **Raman active** but **IR inactive**, while the **bending modes** (mode ν2\nu_2ν2) and **antisymmetric stretching** (mode ν3\nu_3ν3) are **IR active** but **Raman inactive**.
- **Mutual Exclusion**: This illustrates that modes that are **IR active** tend to be **Raman inactive**, and vice versa, in accordance with the **Mutual Exclusion Principle**.

The **Mutual Exclusion Principle** is valuable because it allows for predicting the spectroscopic behavior of molecular vibrations based on their symmetry, helping determine whether a particular vibration will be detected in **IR** or **Raman** spectroscopy.

(ii) The molecule X_2Y has 3 fundamental vibrational frequencies. One is Raman active and two are IR active. Identify the structure of the molecule.

Given the information that the molecule **X_2Y** has three fundamental vibrational frequencies, and:

- **One is Raman active**,
- **Two are IR active**,

This suggests that the molecule has at least one **non-linear structure**.

Analysis of the Vibrational Modes:

- **Non-linear Structure**: Since there are **two IR active** modes, the molecule likely has a **non-linear geometry**. A non-linear molecule typically has **three vibrational modes**, corresponding to different symmetries.
- **IR Active Modes**: These modes involve a change in dipole moment of the molecule. For a vibrational mode to be IR active, the molecule must exhibit a change in dipole moment during the vibration.
- **Raman Active Mode**: This mode involves a change in polarizability of the molecule. For a vibrational mode to be Raman active, it must induce a change in polarizability during the vibration.

From this, we can deduce that **X_2Y** must be a **non-linear** molecule with different symmetries for each vibrational mode.

Possible Structure of X_2Y:

Given the symmetry requirements:

- **X_2Y** could be a **bent molecule** (like **H_2O** or **SO_2**) where the molecule has **two IR active modes** (e.g., bending and asymmetric stretching modes) and **one Raman active mode** (e.g., symmetric stretching or another bending mode).

Thus, the most likely structure of **X_2Y** is a **bent structure**, where the central atom **Y** is bonded to two identical atoms **X**.

Conclusion: The molecule **X_2Y** is likely to have a **bent structure**, similar to **H_2O** or **SO_2**, where one mode is **Raman active** and the others are **IR active**.

8. (a) (i) Explain why the 13C-13C spin splitting is not observed in 13C-NMR spectrum?

(ii) Predict the number of signal and multiplicity of peaks in the 13C spectrum of the following compounds:

a) 2,5-Dimethylhexane

b) Cyclohexanol

(b) (i) What is meant by AX spin system in NMR? Draw a schematic energy level diagram for this system and show the allowed transitions.

(a) (i) Why is the 13C-13C spin splitting not observed in the 13C-NMR spectrum?

In **13C-NMR spectroscopy**, the **13C-13C spin splitting** is typically not observed due to two main reasons:

1. **Low Natural Abundance of 13C**: The natural abundance of **13C** is about **1.1%**, meaning only a very small fraction of carbon atoms in a sample are the 13C isotope. This leads to a low probability of two 13C atoms being adjacent to each other in a molecule. Therefore, the chance of observing **13C-13C spin-spin coupling** (splitting) is very rare.
2. **Wide Chemical Shifts**: The coupling constant between two 13C nuclei is relatively small (on the order of **2-5 Hz**), making it difficult to resolve, especially in complex molecules with multiple carbons. Additionally, the chemical shifts of 13C nuclei are much broader than those of proton NMR peaks, and this broadness makes the subtle splitting due to 13C-13C interactions even harder to observe.

Thus, because of the low probability of two 13C nuclei being adjacent and the weak coupling constant, **13C-13C spin splitting** is typically not resolved in 13C-NMR spectra.

(a) (ii) Predict the number of signals and multiplicity of peaks in the 13C spectrum of the following compounds:

(a) 2,5-Dimethylhexane:

In **2,5-dimethylhexane**, the carbon atoms are arranged in a structure where there are **distinct environments** for the carbon atoms. Let's analyze the different types of carbon environments:

- **Carbons 1 and 6**: Both these carbons are in the same environment because they are attached to a CH_2 group that is connected to two CH_3 groups. There is only **one signal** for these carbons.
- **Carbons 2, 5 (CH3 groups)**: These are the two methyl groups attached to the main chain. Both are in equivalent positions, so they will each contribute **one signal** with **multiplet splitting** from the adjacent carbons.
- **Carbons 3, 4 (CH2 groups)**: These are methylene carbons attached to other carbons. Each of these carbons will give **one signal** and experience **coupling** with adjacent carbons.

Summary for 2,5-Dimethylhexane:

- **Number of signals**: 4 (One for each distinct environment).
- **Multiplicity**:
    - The signal for Carbons 1 and 6 will be a **singlet** because it is not coupled with any other 13C atom.
    - The signals for Carbons 2 and 5 will be **multiplets** due to **splitting from adjacent carbons**.
    - The signals for Carbons 3 and 4 will be **multiplets** due to **splitting from adjacent carbons**.

(b) Cyclohexanol:

For **cyclohexanol**, let's analyze the structure and the carbon environments:

- **Carbons 1, 2, 3, 4, 5, 6** (in the cyclohexane ring): All six carbons in the cyclohexane ring are **equivalent** in a simple chair conformation. However, there will be slight splitting due to the hydrogen atoms attached to these carbons, especially when considering different proton environments. Therefore, this gives **one signal** for the six ring carbons.

- **Carbon 7** (OH-bearing carbon): This carbon is attached to the hydroxyl group and is a distinct environment, so it will produce **one signal**.

Summary for Cyclohexanol:

- **Number of signals**: 2 (One for the ring carbons and one for the hydroxyl-bearing carbon).
- **Multiplicity**:
  - The signal for the ring carbons will be a **multiplet** due to proton coupling.
  - The signal for the OH-bearing carbon will also be a **multiplet** due to proton coupling.

(b) (i) What is meant by the AX spin system in NMR? Draw a schematic energy level diagram for this system and show the allowed transitions.

An **AX spin system** refers to a **spin-spin coupling system** in NMR where **two nonequivalent nuclei** (labeled **A** and **X**) interact through scalar coupling, but they are not coupled with each other. Typically, the coupling is between nuclei of different types, like a **proton** and a **fluorine** or **two different types of protons** (e.g., **CH_2 and CH_3**).

In the **AX spin system**:

- **A** represents one type of nucleus (such as a proton, 1H^1H1H),
- **X** represents another type of nucleus (such as a different proton or a fluorine, 19F^{19}F19F, etc.).

Energy Level Diagram for AX Spin System:

In an **AX spin system**, there are two main components:

- The **A nucleus** and the **X nucleus** both have spin states (+++ or −-−).
- There are **two energy levels** for each spin, and the system can undergo transitions between them. The splitting is caused by the **coupling between the spins**.

Energy Level Diagram:

| (X Spin +1/2, A Spin +1/2)

|

|---------- (Interaction: JAX coupling)

|

| (X Spin -1/2, A Spin +1/2)

|

|---------- (Interaction: JAX coupling)

|

| (X Spin +1/2, A Spin -1/2)

|

|---------- (Interaction: JAX coupling)

|

| (X Spin -1/2, A Spin -1/2)

|

|

In the **AX spin system**, the energy levels split according to the **coupling constant** (JAX), which is the scalar coupling between the two nuclei. Each spin of **A** and **X** will split into **two** peaks due to spin-spin coupling.

Allowed Transitions:

In this system, the transitions that are allowed correspond to the **change in spin states** of the nuclei involved. The allowed transitions can be shown as follows:

- **Transition 1**: From $\mathrm{A}(+1/2)$ and $\mathrm{X}(+1/2)$ to $\mathrm{A}(+1/2)$ and $\mathrm{X}(-1/2)$.
- **Transition 2**: From $\mathrm{A}(+1/2)$ and $\mathrm{X}(-1/2)$ to $\mathrm{A}(-1/2)$ and $\mathrm{X}(+1/2)$.

Thus, in the **AX spin system**, the **splitting** in the NMR spectrum is based on the **coupling constant JAX**, and the transitions occur between the energy levels formed by the coupling of the spins.

9. (a) (i) Calculate the ESR frequency of an unpaired electron in a magnetic field of 3000 G (0.3 T). [Given: g = 2.0023; μB = 9.2741 × 10−24 JT−1; and h = 6.626×10−34 Js]

(ii) Which of the following systems will show electron spin resonance (ESR) spectrum? (i) H (ii) H2 (iii) Na+ (iv) Cl- (v) •CH3 (vi) NO2 (3)

(b) What are different mechanisms that contribute to the relaxation of nuclear spins in the excited state? Explain any one of them.

(a) (i) Calculate the ESR frequency of an unpaired electron in a magnetic field of 3000 G (0.3 T).

To calculate the **Electron Spin Resonance (ESR) frequency**, we can use the following formula:

$$f = \frac{g\mu_B B}{h}$$

Where:

- f is the ESR frequency,
- g is the **g-factor** of the electron (given as **2.0023**),
- μ_B is the **Bohr magneton** ($9.2741 \times 10^{-24}\,\mathrm{J/T}$),
- B is the **magnetic field strength** (given as **0.3 T**),
- h is **Planck's constant** ($6.626 \times 10^{-34}\,\mathrm{J\cdotp s}$).

Now, substituting the given values:

$$f = \frac{(2.0023) \times (9.2741 \times 10^{-24}\,\mathrm{J/T}) \times (0.3\,\mathrm{T})}{6.626 \times 10^{-34}\,\mathrm{J\cdotp s}}$$

Let's calculate the frequency:

$$f = \frac{(2.0023) \times (9.2741 \times 10^{-24}) \times (0.3)}{6.626 \times 10^{-34}} = \frac{5.569 \times 10^{-24}}{6.626 \times 10^{-34}} \approx 8.41 \times 10^{9}\,\mathrm{Hz}$$

Therefore, the **ESR frequency** of an unpaired electron in a **0.3 T magnetic field** is approximately **8.41 GHz**.

(a) (ii) Which of the following systems will show an Electron Spin Resonance (ESR) spectrum?

To determine which systems will show an **ESR spectrum**, we need to understand that ESR detects transitions between different spin states of electrons. **ESR** occurs when there is an **unpaired electron** with a **non-zero magnetic moment**. Thus, systems that contain unpaired electrons are the ones that will show an ESR spectrum.

- **(i) H (Hydrogen)**: Hydrogen (H) does not have an unpaired electron in its ground state (it has a single proton and electron, which are paired). Therefore, **no ESR spectrum** will be observed for **H**.

- **(ii) H_2 (Hydrogen molecule)**: Hydrogen molecules (H_2) have paired electrons in their molecular orbitals, so no unpaired electron is available for ESR detection. Therefore, **no ESR spectrum** will be observed for **H_2**.
- **(iii) Na^+ (Sodium ion)**: The **Na^+ ion** has **no unpaired electron** because it has lost its single valence electron. Therefore, **no ESR spectrum** will be observed for **Na^+**.
- **(iv) Cl^- (Chlorine ion)**: The **Cl^- ion** has an **even number of electrons** and no unpaired electrons, so **no ESR spectrum** will be observed for **Cl^-**.
- **(v) $\bullet CH_3$ (Methyl radical)**: The **methyl radical** ($\bullet CH_3$) has **one unpaired electron**, which makes it suitable for ESR detection. Therefore, **yes**, an **ESR spectrum** will be observed for **$\bullet CH_3$**.
- **(vi) NO_2 (Nitrogen dioxide)**: **NO_2** has an unpaired electron in its **odd number of electrons**. Therefore, **yes**, an **ESR spectrum** will be observed for **NO_2**.

(b) What are the different mechanisms that contribute to the relaxation of nuclear spins in the excited state? Explain any one of them.

In **Nuclear Magnetic Resonance (NMR)** spectroscopy, relaxation refers to the process by which nuclear spins return to their equilibrium state after being disturbed by an external magnetic field. The relaxation mechanisms can be categorized into **two main types**:

1. **Spin-Lattice Relaxation (T_1 Relaxation)**: This process involves the exchange of energy between the nuclear spins and the surrounding lattice or environment. It is also known as **longitudinal relaxation** because the relaxation occurs along the direction of the magnetic field. It is typically slower and is characterized by the **time constant T_1**, which represents the time taken for the spins to return to their equilibrium state.
2. **Spin-Spin Relaxation (T_2 Relaxation)**: This mechanism involves the interaction between different nuclear spins, leading to a transfer of energy between the spins themselves. It is also referred to as **transverse relaxation** because the relaxation occurs in the plane perpendicular to the magnetic field. T_2 is the time constant associated with how long it takes for the spins to lose coherence with each other and return to equilibrium.
3. **Cross-Relaxation**: This occurs when energy is transferred between two spins that are in different states, leading to the relaxation of one spin as a result of the relaxation of another.

Detailed Explanation of T_1 Relaxation (Spin-Lattice Relaxation):

- **Spin-Lattice Relaxation** (T_1 relaxation) is the process by which a nuclear spin, after being excited to a higher energy state, transfers its excess energy to the surrounding **lattice** (the local molecular or atomic environment). This process is called **longitudinal**

relaxation because the nuclear spins return to their equilibrium state along the direction of the applied magnetic field.

- In **T_1 relaxation**, the energy from the excited nuclear spins is dissipated through **collisions** with the surrounding molecules or the lattice, and the energy is transferred to the surrounding system. This causes the spins to gradually return to their lower energy states.
- The rate of spin-lattice relaxation is characterized by the **relaxation time constant** T1, which is the time taken for the nuclear spins to recover **63%** of their equilibrium magnetization after being disturbed. The shorter the T_1 time, the faster the energy transfer between the spins and the lattice.
- **Factors Affecting T_1 Relaxation**:
    - **Temperature**: Higher temperatures increase molecular motion, which enhances the spin-lattice relaxation process.
    - **Viscosity**: In more viscous environments, spin-lattice relaxation tends to slow down because the molecular motion required for energy transfer is limited.
    - **Molecular environment**: The type of surrounding molecules and their electronic properties can influence the T_1 relaxation time. For example, paramagnetic substances or other nuclei with unpaired electrons can shorten T_1 by providing additional relaxation pathways.

10. (a) (i) What is Mossbauer effect?

(ii) The lifetime of 57Fe (excited state) is 1.52 x 107 s. If the excited state is 14.3 keV above the ground state determine the linewidth τ and ratio τ /E.

(b) Write short notes on the following.

(a) Isomer shift (b) Spin-Spin splitting

(a) (i) What is the Mossbauer Effect?

The **Mössbauer Effect** is a phenomenon observed in the absorption and emission of gamma rays by atomic nuclei in a solid without recoil. It was discovered by Rudolf Mössbauer in 1958, and it involves the **resonant absorption** and **re-emission** of gamma rays by a nucleus in a solid lattice. The effect is named after him because it provides highly precise measurements of nuclear energy levels.

The key feature of the Mössbauer Effect is that when an atom in a solid emits or absorbs gamma radiation, it can do so without losing any energy to the recoil of the nucleus. This is

possible because, in a solid, the recoil is absorbed by the lattice, and the energy loss due to recoil is negligible. This effect can occur only for gamma rays emitted or absorbed by a nucleus, and it is most commonly observed in isotopes such as **57Fe** (iron-57), which is widely used in Mössbauer spectroscopy.

The Mössbauer Effect leads to **extremely narrow linewidths** in the gamma-ray spectra, which makes it highly useful for precise measurements of energy levels in nuclei and provides information on the chemical environment and the oxidation state of the atoms.

(a) (ii) The lifetime of 57Fe (excited state) is 1.52 x 10^7 s. If the excited state is 14.3 keV above the ground state, determine the linewidth Γ\GammaΓ and the ratio τE\frac{\tau}{E}Eτ.

The **linewidth** Γ\GammaΓ (also known as the **spectral width**) is related to the lifetime τ\tauτ of the excited state by the **energy-time uncertainty principle**, which states:

$$\Gamma = \frac{\hbar}{\tau}$$

Where:

Now, substituting the given values:

$$\Gamma = \frac{1.055 \times 10^{-34}}{1.52 \times 10^{7}} = 6.94 \times 10^{-42}\,\mathrm{J}\backslash\mathrm{cdotps}$$

Next, to find the **ratio** $\frac{\tau}{E}$, we can use the following relationship:

$$E = 14.3\,\mathrm{keV} = 14.3 \times 10^{3}\,\mathrm{eV} = 14.3 \times 10^{3} \times 1.602 \times 10^{-19}\,\mathrm{J}$$

$$E = 2.29 \times 10^{-15}\,\mathrm{J}$$

Now, the ratio $\frac{\tau}{E}$ is:

$$\frac{\tau}{E} = \frac{1.52 \times 10^{7}}{2.29 \times 10^{-15}} = 6.64 \times 10^{21}\,\mathrm{s/J}$$

Therefore:

- The **linewidth** Γ is $6.94 \times 10^{-42}\,\mathrm{J}\backslash\mathrm{cdotps}$.
- The **ratio** $\frac{\tau}{E}$ is $6.64 \times 10^{21}\,\mathrm{s/J}$.

(b) Write short notes on the following:

(a) Isomer Shift:

The **isomer shift** is a key feature in **Mössbauer spectroscopy** and refers to the shift in the energy of gamma rays due to the interaction between the **nuclear charge distribution** and the **electron cloud** surrounding the nucleus.

When a nucleus is in an excited state and interacts with surrounding electrons, the **electronic environment** around the nucleus affects the energy levels of the nucleus. This results in a shift in the energy of the gamma radiation that is absorbed or emitted by the nucleus, known as the **isomer shift**.

The magnitude of the isomer shift is related to:

1. The **oxidation state** of the atom,
2. The **electron density** around the nucleus,
3. The **chemical bonding** in the material.

- **Higher electron density** around the nucleus leads to a **larger isomer shift**, because the electron cloud shields the nucleus, reducing the effective nuclear charge seen by the gamma rays.
- **Oxidation state** changes also influence the electron density, thus affecting the isomer shift.

In **57Fe Mössbauer spectroscopy**, the isomer shift is often used to distinguish between different **oxidation states** of iron (such as Fe^{2+} and Fe^{3+}) and to provide insights into the **chemical environment** around the iron atom.

(b) Spin-Spin Splitting:

Spin-spin splitting, also known as **coupling**, is a phenomenon observed in NMR (nuclear magnetic resonance) spectroscopy, where the signal of a nucleus is split into multiple peaks due to the interaction with neighboring non-equivalent nuclei. This splitting occurs because the magnetic field experienced by a nucleus is influenced by the spins of nearby nuclei.

When two nuclei are in close proximity and have non-zero spins, the magnetic field due to one nucleus can affect the energy levels of the other nucleus. This results in multiple resonance frequencies, leading to **multiplets** in the NMR spectrum.

In the case of **proton NMR (1H-NMR)**:

- If a proton (H) is coupled to one or more neighboring protons, the signal will be split into a **multiplet**.

- The number of peaks in the multiplet corresponds to the number of neighboring protons plus one, according to the **n+1 rule**.

For example, if a proton is coupled to two equivalent protons, the signal will be split into a **triplet** (n = 2, so n+1 = 3). If it is coupled to three equivalent protons, the signal will be split into a **quartet** (n = 3, so n+1 = 4).

The **coupling constant** (denoted as JJJ) defines the spacing between the peaks in the multiplet, and it is measured in **Hz**. The **spin-spin coupling** provides valuable information about the **proximity** and **environment** of nuclei in the molecule, helping in the structural elucidation of compounds.

In **13C-NMR**, spin-spin coupling also occurs between carbon nuclei and protons, leading to further splitting patterns that can help in identifying the molecular structure.

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